

Bond-Ordering Model for the Glass Transition

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We consider the idea of bond ordering as a model for the glass transition; a generic covalently bonded liquid may substantially reduce its energy through bond ordering, without undergoing significant structural order. This concept is developed for a model system using quantities such as a bond order-parameter and susceptibility which provide a new identification for the calorimetric glass transition temperature. Monte Carlo simulation results exhibit bond ordering at intermediate temperatures uncorrelated with any long-range structural ordering. Also discussed are various other implications of bond-ordering model for the glass transition.

I. INTRODUCTION

The problem of glass formation is a classic one in physics and materials science. Viewpoints break down into kinetic explanations of an arrested liquid, and phase transitions with some kind of order parameter. Discussions have approached the glass transition in terms of the fragmentation of small structural units,¹ the agglomeration of clusters through chemical bonds,² or correlations between different metastable equilibrium states representing distinct configurations or rearrangements of the system.³ In addition, attempts have been made to incorporate frustration in local bond ordering in a glass through the introduction of a local order parameter describing locally preferred arrangements of liquid molecules, which, in general, are not consistent with the crystallographic symmetry favored by density ordering.⁴ In this model the frustration arises from competition between density ordering and local bond ordering, explaining why some molecules crystallize easily without vitrification, while others easily form glasses without crystallization. Another approach, using computer simulations, introduces a displacement-displacement correlation function as a measure of the local configurational order which grows as the temperature is lowered toward the glass transition.⁵ Finally, the role of fluctuations has been reviewed in general fashion with both theoretical and experimental evidence for heterogeneity at the glass transition.⁶ We would like to introduce a model of positional glass which incorporates many of these ideas in simple form.

First we recall some of the basic structural features of typical network-glass-formers like silica. Vitreous silica is made up of SiO_4 tetrahedra just like the crystalline phase, quartz. Thus, molecular structure for the two different phases of silica, *i.e.* crystalline and amorphous, are very much alike, with the major exception of n.n.n. distance $\text{Si}_1\text{-Si}_2$ which may be specified in terms of the Si-O-Si bond angle. The distribution of Si-O-Si bond angles β as determined by Mozzi and Warren for vitreous silica is shown in Fig. 1.⁷ From the bond angle distribution

$V(\beta)$, it is clear that the $\text{Si}_1\text{-Si}_2$ distances vary significantly, which in fact is the primary source of topological disorder. Yet the bond angle β is confined to within roughly 30° of its most probable value *viz* 144° . Clearly, the variation in β is large enough to suppress the long-range order (LRO) characterizing the crystalline phase, and yet small enough to maintain the medium-range order (MRO) which extends to about 10RA . Hence, we note that ordering in n.n. and n.n.n. distances or bond lengths is well maintained in spite of the fact that vitreous silica is devoid of any substantial structural order. Similar structural properties are observed in various other network glasses such as B_2O_3 and GeO_2 . This observation is striking enough to indicate a strong role for the ordering of bonds in a proper microscopic model for the glass transition. The bond ordering can be viewed as being brought about by the local reorientations of molecular clusters as suggested in the theory of Adam and Gibbs.⁸ The idea is that supercooled liquids do not necessarily need to undergo structural ordering in order to achieve local equilibrium. In fact, local rearrangements of molecular clusters can lead to substantial lowering in the internal energy of an entire sample through reducing bond energies at the local level, which is the primary reason for the ordering of n.n. and n.n.n. distances, or alternatively the bond-angle degrees of freedom, in amorphous materials.

A model for the glass transition incorporating small structural units or fragments was proposed by M. Suzuki *et al.*¹. In this fragmentation model noncrystalline solids are assumed to be assemblies of pseudo-molecules—a pseudo-molecule being a cluster of atoms having a disordered lattice in which there are no definite defects such as under- or over-coordinated atoms. As temperature increases, bond breaking intensifies at the boundaries of such clusters where the bonds tend to be weak. The bond breaking mechanism arising from the thermal excitation of electrons from bonding to antibonding energy states, causes the noncrystalline solid to fragmentize, with the average fragment size decreasing as the temperature increases. Consequently, material begins to show viscous

flow when average fragment size reaches a critical value. The model is shown to have some success in describing the temperature dependence of viscosity and the variation in transition temperature with heating rate for a-Si. The origin of pseudo-molecules in the cooling process, however, is not addressed in the fragmentation model.

In the following we consider a microscopic model for the glass transition which is general enough to be applicable to various types of glass-forming systems with widely differing bonding schemes and chemical compositions. We would like to treat glass transition as a phenomenon that finds similar description whether a liquid is cooled or heated through the transition. The focus of bond-ordering model is the bonds linking neighboring atoms rather than the atoms themselves. In other words, a bond is treated as a distinct object in its own right, possessing internal degrees of freedom or electronic states. The internal state of a bond is governed by the separation of the participating atoms. The term bond-ordering refers to the process of relaxation of bonds into their low-lying internal energy states, facilitated by the cooperative rearrangements within molecular groups. Bond ordering, therefore, may be viewed as some form of ordering in energy space. The important point that we would like to bring home, however, is that such an ordering can be achieved without need for any significant structural order. To this effect, we have provided results from Monte Carlo (MC) simulations of the model Hamiltonian which couples the coordinates of ions to the electronic states of electrons, as for a typical covalently bonded network glass. The simulations make clear the possibility of local ordering of bonds, uncorrelated with any kind of long-range structural ordering.

Sec. II of this article contains the theoretical background regarding the covalently-bonded systems. In Sec. III we describe the model Hamiltonian. Some new definitions in terms of mathematical expressions for various structural and bond-related quantities of interest, are introduced in Sec. IV. The simulation procedure and results are discussed extensively in Sec. V. Sec. VI contains the concluding remarks and a summary of the main ideas introduced in this article.

II. THEORETICAL BACKGROUND

Glass-forming liquids include covalently-bonded network glasses, coordination-constrained metallic glasses and systems made of more complex organic molecules or polymer. Here we take the view that the interaction between constituent atoms or molecular units is given by an effective potential which characterizes their positional and orientational interaction. In particular for covalent materials the interactions may be reasonably described in terms of basis states of degenerate *s* and *p* orbitals on each atom. Linear combinations of orbitals on neighboring atoms then lead to bonding and antibonding states

which describe the interactions between atoms. The occupation of the bonding state by one to two electrons results in a lowering of the electronic energy relative to the atomic levels. This covalent bond provides the structural constraint on the relative position of the two atoms.

In order to be more specific we consider a general Hamiltonian for a covalently bonded network glass. We start first with a general formulation of the Hamiltonian for a typical glass-forming liquid. Although these systems are often treated in a classical formulation, in fact, the bonding between atoms in a network glass, as well as the coordination in metallic glasses arise from quantum mechanical considerations. The many-body Hamiltonian may be written in the form:

$$H = H_{ii} + H_{ie} + H_{ee} , \quad (1)$$

where H_{ii} is the interaction between ions in the liquid, H_{ie} is the ion-electron interaction, and H_{ee} is the interaction between electrons. The usual approach to solving this type of many-body problem is to exploit the separation of time scales inherent in the Born-Oppenheimer approximation: solve for the electronic states regarding the ionic coordinates as parameters, then vary the ionic coordinates to minimize the energy or extract the electron-phonon interaction, etc. For a covalent material like most network glasses, the electronic states are reasonably approximated by forming bonding and antibonding states from the atomic *s* and *p* orbitals. The available electrons are then apportioned to the lowest bonding states to obtain the ground state of the system. The bonding and antibonding energies, depend on distance or separation as shown schematically in Fig. 1: the bonding state has a minimum at an ion-ion distance r_0 , while the antibonding state is repulsive at all distances. This may be thought of as a tight-binding approximation to the actual electronic structure of a glass. A bond, is a bonding state occupied by two electrons and is strongest (or has lowest energy) when the distance between ions is near r_0 . On the other hand, a bond missing an electron due to a thermal fluctuation or a transition of the electron to the antibonding state, corresponds to a broken bond. In this tight-binding representation of bonds, the Hamiltonian may be expressed as in Eq. (1), a more detailed expression of which is derived in the next section.

III. MODEL HAMILTONIAN

The potential energy of a pair interaction may be expanded in the displacement x from the equilibrium:

$$U(x) = U_0 + \frac{x^2}{2!} U_0'' + \frac{x^3}{3!} U_0''' + \dots , \quad (2)$$

where the coefficients are evaluated at equilibrium separation. Dropping the constant term which plays no role, and in the harmonic approximation, we get:

$$U(x) = \frac{x^2}{2} U_0'' . \quad (3)$$

For our lattice model we identify $x = |\mathbf{R}_i - \mathbf{R}_j|$, where \mathbf{R}_i and \mathbf{R}_j are the displacements from the equilibrium of the atoms assigned to the i th and j th n.n. sites, respectively. Hence, with the idealizing constraint that all displacements are of same magnitude $|\mathbf{R}|$, *i.e.* $|\mathbf{R}_i| = |\mathbf{R}_j| = |\mathbf{R}|$, we have:

$$U(|\mathbf{R}_i - \mathbf{R}_j|) = |\mathbf{R}|^2 U_0'' \left(1 - \hat{\mathbf{R}}_i \cdot \hat{\mathbf{R}}_j\right) . \quad (4)$$

Letting $J = |\mathbf{R}|^2 U_0''$, we obtain the following Hamiltonian for a system of atoms interacting through n.n. coupling:

$$\tilde{\mathcal{H}} = -J \sum_{\langle i,j \rangle} \left(\hat{\mathbf{R}}_i \cdot \hat{\mathbf{R}}_j \right) . \quad (5)$$

This is clearly of the same mathematical form as the q -state clock model Hamiltonian, when the displacement degrees of freedom are taken to be discrete.

The interaction Hamiltonian we used for our MC simulations, is the following:

$$\begin{aligned} \mathcal{H} &= -J \sum_{\langle i,j \rangle} \left(\hat{\mathbf{R}}_i \cdot \hat{\mathbf{R}}_j + 1 \right) n_{ij} \\ &= -J \sum_{\langle i,j \rangle} (\cos \theta_{ij} + 1) n_{ij} , \end{aligned} \quad (6)$$

where $\theta_{ij} = \frac{2\pi}{8}(s_i - s_j)$, with $s_i, s_j = 1, 2, \dots, 8$. The s_i 's are integer labels for various possible displacements of an atom from its equilibrium lattice site i . The quantity n_{ij} should be regarded as the bonding-electron occupation number for a (possible) bond, linking n.n. sites i and j . A bond may or may not be broken depending on whether the corresponding n_{ij} takes on the values 0, or 1, respectively. The value taken by n_{ij} depends on the number of bonding-electrons made available to the system—this is an input parameter to the simulation code—and the relative values of energies of the n.n. interactions. Bonds with lower values of energy are more likely to have bonding-electrons. Interesting effects are observed with a bonding-electron (hole) concentration of about 60% (40%) and that is what we report later in this article. As we shall see shortly, the net effect of holes is to suppress the XY -like transition occurring for clock models with $q > 4$, and hence allowing us to observe the behavior of a disordered system with lowering of the temperature.

IV. SOME NEW DEFINITIONS

In Sec. I we defined bond ordering as that process involving relaxation of bonds into their low-lying internal energy states. There are a few more physical parameters relevant to our discussion which are defined in this section and are considered in context of the glass transition phenomenon.

A. Bond Order-Parameter

We introduce bond order parameter (or bond magnetization) as a measurable physical property that indicates the extent of bond ordering prevailing in a physical system. We begin with considering a two dimensional system of 4-fold coordinated atoms interacting through n.n. coupling of strength J . The bond magnetization of such a system is significant when bonds are in their low-lying energy states (as for a bond-ordered low temperature phase), and negligible when bonds are distributed among all possible energy states with uniform probability which is indeed the case when the thermal energy is far in excess of the coupling strength J . To construct an expression for the bond magnetization of such a system, every n.n. pair of atoms is characterized by a vector $\hat{\mathbf{B}}_{ij}$ the purpose of which is to characterize the interaction energy. $\hat{\mathbf{B}}_{ij}$ is specified via the angle it makes with an arbitrary fixed axis in the plain of the system, ϕ_{ij} . The angle ϕ_{ij} is written in terms of bond energy as:

$$\phi_{ij} = \pi \frac{\epsilon_{ij}}{J} , \quad -J \leq \epsilon_{ij} \leq J , \quad (7)$$

where J is n.n. coupling strength, ϵ_{ij} is the bond energy and $-\pi \leq \phi_{ij} \leq \pi$. An expression that fulfills all the requirements of an extensive bond magnetization is the following:

$$\begin{aligned} M_b &= \left\langle \left(\sum_{\langle i,j \rangle}^{2N} \hat{\mathbf{B}}_{ij} \right)^2 \right\rangle^{1/2} \\ &= \left(\sum_{\langle i,j \rangle}^{2N} \sum_{\langle m,n \rangle}^{2N} \left\langle \hat{\mathbf{B}}_{ij} \cdot \hat{\mathbf{B}}_{mn} \right\rangle \right)^{1/2} , \end{aligned} \quad (8)$$

where angular braces stand for thermal average and N is the total number of atoms in the system. In terms of bonds' energies, the expression for intensive bond magnetization of the system; $m_b = M_b/2N$, may be written as:

$$m_b = \frac{1}{2N} \left(\sum_{\langle i,j \rangle}^{2N} \sum_{\langle m,n \rangle}^{2N} \left\langle \cos \left[\frac{\pi}{J} (\epsilon_{ij} - \epsilon_{mn}) \right] \right\rangle \right)^{1/2} . \quad (9)$$

The normalization is chosen such that $0 \leq m_b \leq 1$.

B. Bond Susceptibility

Bond susceptibility is the response function associated with bond magnetization M_b and its thermodynamic conjugate field H_b , called bond ordering field.⁹ The exact physical nature of H_b is not yet known to us; however, bond susceptibility can still be calculated without appealing to a knowledge of H_b .

The change in Gibbs free energy in an infinitesimal bond ordering process may be written in terms of the newly introduced parameters M_b and H_b , as in the following:

$$dG = -SdT - M_b dH_b. \quad (10)$$

Eq. (10) can serve as starting point for incorporating M_b into the thermodynamics of disordered systems. Bond susceptibility apart from a normalization will therefore be given by:

$$\chi_b = \frac{\partial M_b}{\partial H_b} = -\frac{\partial^2 G}{\partial H_b^2}. \quad (11)$$

Starting with Eq. (11), one may readily obtain an expression for the bond susceptibility in terms of fluctuations in the bond magnetization:

$$\chi_b = (\langle |\mathbf{M}_b|^2 \rangle - \langle |\mathbf{M}_b| \rangle^2) / 2Nk_B T, \quad (12)$$

where $\mathbf{M}_b = \sum_{i,j}^{2N} \hat{\mathbf{B}}_{ij}$. Eq. (12) is properly normalized to the number of n.n. bonds $2N$ for a system of N atoms with periodic boundary conditions, and is used for calculating bond susceptibility via MC simulations.

This rather abstract entity, the bond susceptibility, describes the tendency of a system for bond ordering and provides the basis for a new identification of glass transition temperature.

C. New Identification for T_g

Following the previous discussion one can trace the origins of MRO characteristic of the vitreous state in the local ordering of bonds, which becomes most intense at some particular temperature T_g . This brings us to another identification for the calorimetric glass transition temperature, which particularly applies to fragile and intermediate class of the glass-forming liquids.¹⁰ In glass transition region, bond susceptibility of a supercooled glass-forming liquid reaches a maximum. This also implies that specific heat must display a maximum in the glass transition region because of the large energy fluctuations associated with the intense ordering of bonds. In view of this, the transition peak in the experimentally measured specific heat of various fragile and intermediate glass-formers can be regarded as an artifact of intense bond ordering or strong fluctuations in the number of bonds in each energy state occurring at glass transition. Hence, we propose a new identification for T_g as that temperature corresponding to maximum of bond susceptibility of a supercooled liquid nearing configurational arrest.

Having given an explanation for the specific heat peak at the glass transition, it doesn't seem improper to consider the unexpected linear behavior of specific heat at very low temperatures.¹¹ Work by Hunklinger *et al.* gives

strong evidence that the low temperature anomalous properties of amorphous materials arise mainly from two-level systems and not from the multi-level vibrational degrees of freedom associated with the atoms.¹² The energy gaps Δ of the two-level systems are supposed to vary with uniform probability in some range $0 \leq \Delta \leq \Delta_0$, where $\Delta_0 \approx 1K$.^{13,14} These low energy excitations may be attributed to the bond ordering process at low temperatures. In disordered systems, whether supercooled liquids or glass, bonds continuously relax into more stable internal energy states with lowering of the temperature. At very low temperatures certain number of bonds may be seen to act like two-level systems with varying energy gaps. Bond ordering process at low temperatures is therefore a possible explanation for the low temperature anomalous properties exhibited by amorphous materials.

D. Structural Magnetization and Susceptibility

Structural magnetization is a measure of the conventional LRO a system may possess. For the system we are considering the displacement of an atom from its designated equilibrium lattice site i , is characterized with \mathbf{R}_i . Further idealizing the system by assuming that displacements are of same magnitude $|\mathbf{R}|$, we can express extensive structural magnetization as in the following:

$$M_s = \left\langle \left(\sum_{i=1}^N \hat{\mathbf{R}}_i \right)^2 \right\rangle^{1/2}, \quad (13)$$

where $\hat{\mathbf{R}}_i = \mathbf{R}_i / |\mathbf{R}|$. The intensive (or normalized) structural magnetization is given by; $m_s = M_s / N$, where $0 \leq m_s \leq 1$. The analogy between structural magnetization and magnetization of a magnetic system, is rather obvious. In fact, we can use this analogy to express structural susceptibility in terms of fluctuations in structural magnetization, as follows:

$$\chi_s = (\langle |\mathbf{M}_s|^2 \rangle - \langle |\mathbf{M}_s| \rangle^2) / Nk_B T, \quad (14)$$

where $\mathbf{M}_s = (\sum_i R_i^x, \sum_i R_i^y)$. Structural susceptibility is the response function describing the tendency for structural ordering.

E. Order-Parameter for Glass

We would like to address at this point a possible order parameter (or order parameter density) for supercooled liquids and glass, that also serves as yet another distinction between fragile and strong classes of the glass-forming liquids. This will simply be the bond magnetization if one is considering strictly a liquid \leftrightarrow glass transition.

Many of the theories describing glass transition phenomenon, assume that there is a single parameter which

characterizes glass. This assumption is believed to be inaccurate.¹⁵ Prigogine and Defay have shown that in general the ratio of the discontinuities in second-order thermodynamic quantities; isothermal compressibility, heat capacity at constant pressure, and coefficient of thermal expansion:

$$R = \frac{\Delta\kappa_T \Delta C_p}{TV(\Delta\alpha)^2}, \quad (15)$$

is equal to unity if a single order parameter characterizes the underlying thermodynamic transition, but if more than one order parameter is involved, then $R > 1$.¹⁶ The latter seems to describe most glasses. In view of this, we consider a two parameter description of glass which involves two of the parameters described earlier, namely, the structural magnetization m_s and the bond order parameter m_b . We require for amorphous solids that the structural LRO vanishes while the bond magnetization remains significantly large. The requirement of the vanishing of structural LRO, is meant to characterize the liquid-like attributes of the amorphous systems. Yet large values for bond order parameter is a solid-like attribute that should serve to distinguish the glass from the liquid phase.

Clearly, in case of strong glass-formers characterized with strong covalent bonds, the values for bond order parameter above and below the transition must be quite comparable. However, in case of fragile systems the liquid undergoes substantial bond ordering at the transition mainly due to the nondirectional nature of their chemical bonds. As a result bond magnetization is expected to vary rather significantly for the fragile class. Originally, the labels strong and fragile were introduced to refer to the ability of a liquid in withstanding changes in MRO with temperature.¹⁰ In context of bond-ordering model, these labels will be referring to the ability of a liquid to withstand changes with temperature in bond magnetization m_b . It is worthwhile to mention that in this scheme an ideal glass may be characterized as being maximally bond ordered which should also imply the least possible energy.

V. SIMULATION: PROCEDURE AND RESULTS

Clock models have been investigated in some detail, both analytically and through numerical methods.^{17–19} Previous Monte Carlo works, have examined the behavior of 2D clock systems with various values of the parameter q . The important results are that for $q \leq 4$ the system exhibits one second-order transition, but for $q > 4$ two Kosterlitz-Thouless (KT) transitions²⁰ are present. The upper transition temperature is believed to have a value approximately equal to the KT transition temperature for the continuous model,²¹ $T_c = 0.89 J/k_B$. As q

increases, the lower transition temperature ($\propto 1/q^2$) approaches zero, leaving just one KT transition for the 2D XY-model.

For model Hamiltonian we consider Eq. (6), which in fact is a bond-diluted version of $q=8$ state clock model, involving n.n. interaction with antibonding electronic state. For our purpose, the eight possible orientations must be interpreted as the possible displacements of an atom from its designated equilibrium lattice site, with every atom's displacement being the same if the system were in a ordered configuration.

The standard MC importance-sampling method was used to simulate the behavior of the system on $L \times L$ square lattices with periodic boundary conditions. We performed simulations on lattices of size $L = 12, 20, 32$, and 50 . Preliminary work was carried out on systems of size $L = 12$. In every case the temperature was lowered in steps of $0.05 J/k_B$, starting with initial value $T = 2.00 J/k_B$. The system was initialized in random configuration suitable for high temperatures where it is known to be disordered. At every temperature system was allowed to equilibrate through a few hundred Monte Carlo steps per site (MCS). The data points were then acquired by averaging over 40,000 MCS. The data were accumulated in several bins, and binned averages were used to obtain error estimates for the calculated means and also to monitor the state of equilibrium. For most cases the estimated statistical errors were less than 2% of the calculated mean values. In order to test our code, we simulated $q = 6$ state clock model and compared our results with the extensive literature available on the subject.^{17,18} To our satisfaction the agreements were impressive. As a note on the calculation of internal energy, the (possible) bonds were sorted out in ascending order of energy at every time step and were given bonding-electrons in that order.

Many of the quantities calculated have been already discussed and given explicit mathematical definitions in Sec. IV. In addition, specific heat was obtained from fluctuations in the total energy:

$$C = (\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2) / 2Nk_B T^2. \quad (16)$$

The bond-related quantities; bond order parameter, bond susceptibility, internal energy and specific heat are normalized to the number of n.n. bonds $2N$, for a system of size $N = L^2$ with periodic boundary conditions. On the other hand the structural properties, *i.e.* structural magnetization and susceptibility are normalized to the system size N . Results correspond to a hole concentration of 40%.

Perhaps the most interesting feature of the results is the conspicuous peak in bond susceptibility, shown in Fig. 2, which is an indication of bond ordering, uncorrelated with any long-range structural ordering as is evident from structural magnetization and susceptibility seen in Figs. 3, and 4. Finite size effects are quite evident. The temperature at which bond susceptibility reaches

its maximum value is estimated to be $0.9 J/k_B$, consistent with the KT transition temperature. At exactly the temperature where bond susceptibility maximum occurs, one observes a maximum in specific heat shown in Fig. 5, which should be attributed to large energy fluctuations associated with the ordering of bonds. Indeed, experimental measurements of heat capacity for covalently bonded fragile systems such as As_2S_3 and B_2O_3 , exhibit similar peaks at glass transition which therefore suggest bond ordering nature for the glass transition. The internal energy for various system sizes is shown in Fig. 6, displaying steep slope in bond ordering region.

Fig. 7 contains the variation of bond magnetization with temperature. In bond ordering region, bond magnetization increases rapidly with decreasing temperature in spite of the fact that structural magnetization stays fairly constant there. This behavior testifies to the earlier assertion that a system can undergo substantial bond ordering and hence largely reduce its internal energy without undergoing any significant structural ordering.

Unlike the behavior expected from q -state clock model in 2D, structural susceptibility (Fig. 4) does not exhibit singular behavior at intermediate temperature range hence ruling out the possibility of long-range cooperative structural ordering. This behavior of structural susceptibility may be seen in view of the large concentration of holes or bond dilution.

VI. SUMMARY

We have investigated the existence of order associated with bonds, in amorphous systems of interest such as vitreous silica. Through our MC simulations, it is found that bond ordering may occur independently of structural ordering. Bond ordering implies ordering in n.n. and n.n.n. distances and thus leads to MRO, which is a key aspect of the vitreous state.

An order parameter for supercooled liquids and glasses is introduced. In case of liquid \leftrightarrow glass transition bond magnetization m_b may be fruitfully employed in the thermodynamics of glass and any calculation that may involve coarse-grained parameters. In addition, a new identification for glass transition temperature is afforded through the variation with temperature of the bond susceptibility.

As a last remark, the sharp rise in the viscosity of glass-forming liquids when cooled toward glass transition,¹⁰ may be viewed in terms of strengthening of bonds. The fragile glass-formers undergo significant bond ordering through the transition and for that reason their viscosity rises dramatically, as opposed to the smooth Arrhenius-like behavior of viscosity exhibited by strong glass-forming liquids.

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FIG. 1. The distribution of Si-O-Si bond angle, measured by Mozzi and Warren.⁷

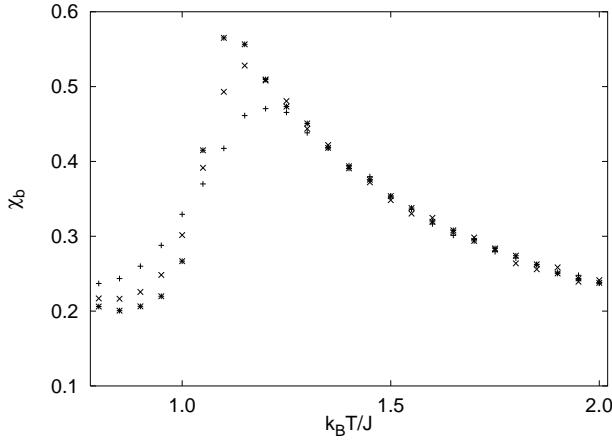


FIG. 2. Plot of bond susceptibility vs. temperature for three different system sizes; 20^2 (+), 32^2 (x), and 50^2 (*).

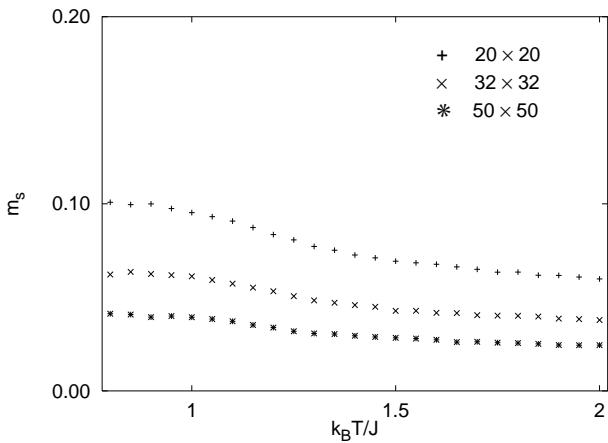


FIG. 3. Plot of structural magnetization vs. temperature. Each curve is normalized to the corresponding system size N .

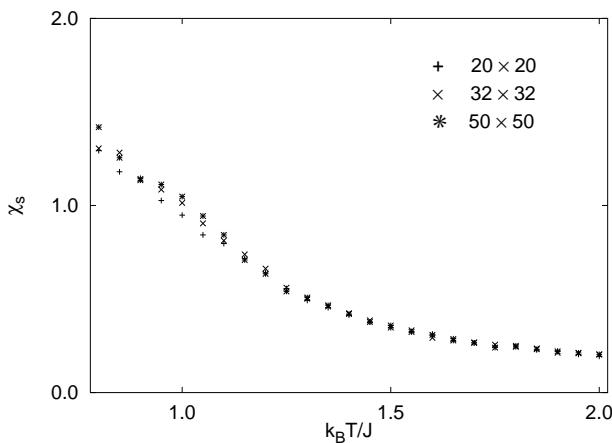


FIG. 4. Variation of structural susceptibility with temperature. Clearly, there is no indication of long-range structural ordering in the temperature range shown.

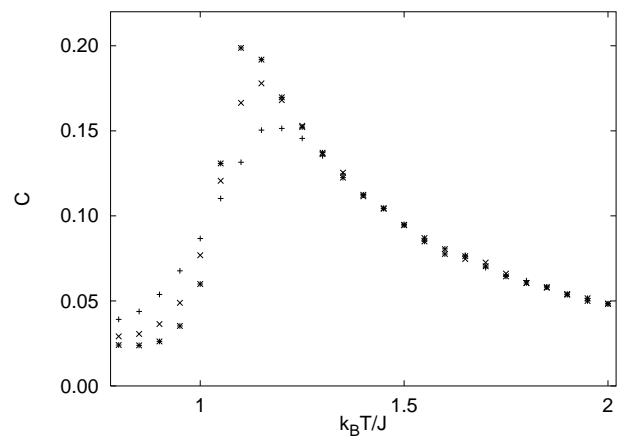


FIG. 5. Specific heat as a function of temperature for three different system sizes; 20^2 (+), 32^2 (x), and 50^2 (*).

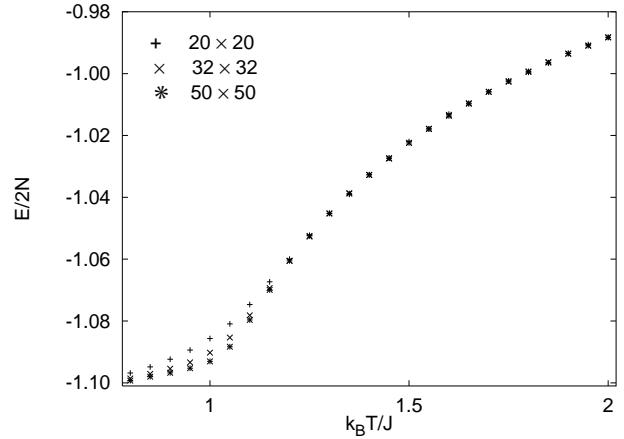


FIG. 6. Energy per bond as a function of temperature. The total energy E is in units of the coupling J .

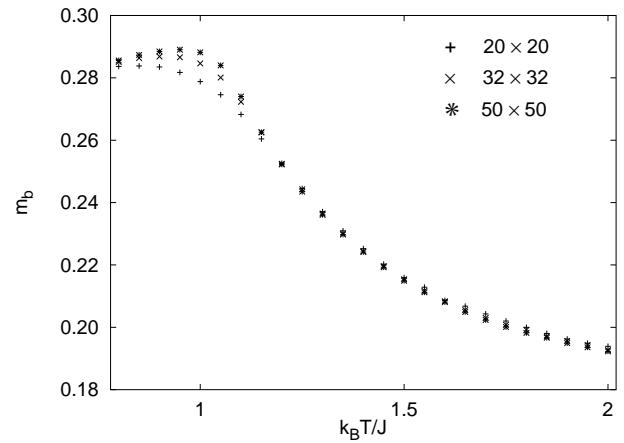


FIG. 7. Plot of bond magnetization vs. temperature. There appears a sharp variation due to bond ordering, uncorrelated with any long-range structural ordering.